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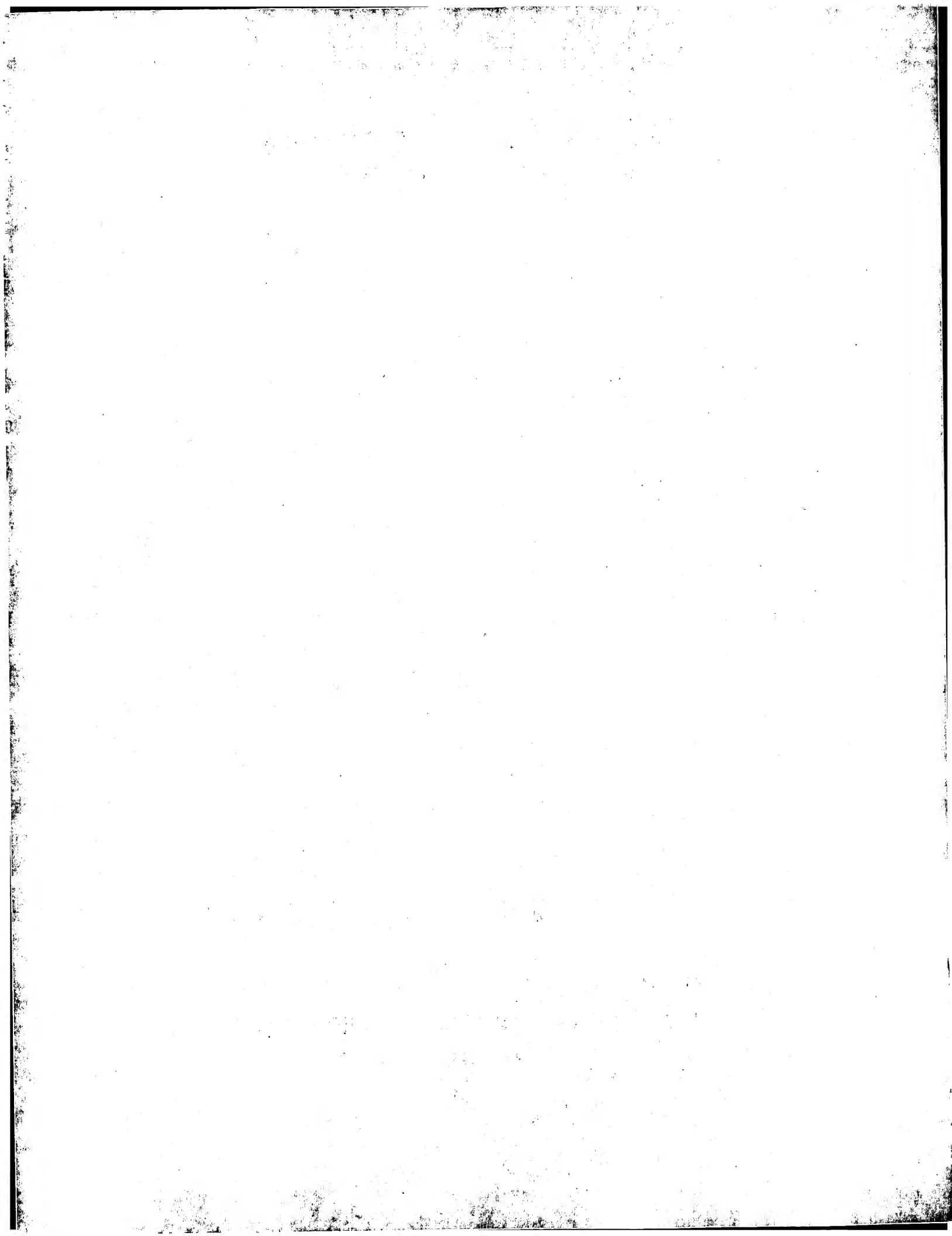
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Preparation and Properties of Water-borne Polyurethanes

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Abstract: Following a prepolymer mixing process, polyurethane (PU) anionomer dispersions were prepared from polyethylene adipate glycol (PEA), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) and dimethylol propionic acid (DMPA) as a potential ionic centre. Effects of prepolymer molecular weight, PEA molecular weight, hard segment content, DMPA content, degree of neutralization and mixed diisocyanates have been studied in terms of particle size and viscosity of emulsion, and surface, mechanical and dynamic mechanical properties of the emulsion-cast films. Particle size decreased and emulsion viscosity increased with increase in prepolymer molecular weight and PEA molecular weight, DMPA content, the degree of neutralization and IPDI content in mixed isocyanate systems. The decrease in particle size was due to increased chain flexibility and/or hydrophilicity of the PU. The mechanical and dynamic mechanical properties of the PU ionomer dispersions were interpreted in terms of soft segment-hard segment phase separations, hard segment content, chain flexibility and coulombic forces.

Key words: polyurethanes, anionomer dispersions, structure-property correlation, mechanical properties, dynamic mechanical properties.

INTRODUCTION

Since aqueous dispersions of polyurethane (PU) are non-toxic, non-flammable and do not pollute the air, they have been widely used in coatings and adhesives for flexible substrates (textile, leathers, papers and rubber), wood and glass fibres.¹⁻⁵ In addition, chain extension of NCO-terminated prepolymers has been carried out in the form of dispersions. Therefore it has been possible to set the molecular weight at any level without the viscosity being impaired.

PU dispersions can be prepared in the form of ionomer and non-ionomers. Advantages and disadvantages of the two types of dispersion are well documented in the literature.^{1,6,7} Synergistic effects of ionic and non-ionic dispersions have also been obtained by combining ionic and non-ionic hydrophilic groups in the same PU.⁶

Like solvent-borne PUs, the properties of PU ionomers are largely governed by the soft segment-hard

segment phase separation.⁸⁻¹⁰ Factors influencing the phase behaviour include segmental polarity difference, segment length, crystallizability of each segment, intra- and inter-segment interactions and overall composition. The existence of hard segments may give PU ionomers their excellent mechanical properties. An elevation of soft segment glass transition temperature (T_g) is observed as a result of the presence of dissolved hard segments.^{11,12} It is generally known that polyester soft segments contribute to phase mixing by hydrogen bonding between the oxygen of the ester group and the NH group of the urethane linkage.¹³ Many previous investigations have reported a microdomain structure in segmented PU.¹⁴⁻¹⁷ However, work on PU ionomers in the past was mainly done in industrial laboratories,¹⁸ and systematic data on structure-property relationships are sparse in the open literature.

This paper is part of our continuing effort to elucidate the structure-property relationships of PU ionomer dispersions.¹⁹⁻²³ Because of the diverse variables determining phase morphology and property, no straightforward approach seems to exist.

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TABLE 1. Formulations for the synthesis of water-born polyurethane

M_p	Polyol		IPDI (wt%)	IPDI/HDI	DMPA (wt%)	BD (wt%)	TEA		TETA (wt%)	Hard content (%)	Water (g)
	\bar{M}_n	Content (wt%)					neutralization	content (wt%)			
(a) Variation of molecular weight of prepolymer (M_p) and polyol (\bar{M}_n)											
3 000	1 000	63.74	27.84		3.5	0	100	2.64	2.285	36.26	160
	1 250	63.74	27.01		3.5	0.82	100	2.64	2.286	36.26	160
	1 500	63.74	26.47		3.5	1.37	100	2.64	2.286	36.26	160
	1 750	63.74	26.08		3.5	1.75	100	2.64	2.287	36.26	160
	2 000	63.74	25.80		3.5	2.04	100	2.64	2.287	36.26	160
5 000	1 000	63.74	27.69		3.5	1.05	100	2.64	1.384	36.26	160
	1 250	63.74	26.86		3.5	1.88	100	2.64	1.385	36.26	160
	1 500	63.74	26.32		3.5	2.42	100	2.64	1.385	36.26	160
	1 750	63.74	25.93		3.5	2.81	100	2.64	1.385	36.26	160
	2 000	63.74	25.64		3.5	3.09	100	2.64	1.386	36.26	160
7 000	1 000	63.74	27.62		3.5	1.51	100	2.64	0.993	36.26	160
	1 250	63.74	26.80		3.5	2.33	100	2.64	0.993	36.26	160
	1 500	63.74	26.25		3.5	2.88	100	2.64	0.994	36.26	160
	1 750	63.74	25.87		3.5	3.26	100	2.64	0.994	36.26	160
	2 000	63.74	25.58		3.5	3.55	100	2.64	0.994	36.26	160
(b) Variation of hard content											
5 000	2 000	73.70	18.77		3.5	0	100	2.64	1.390	26.26	160
		68.72	22.21		3.5	1.55	100	2.64	1.390	31.28	160
		58.75	29.09		3.5	4.64	100	2.64	1.383	41.25	160
		53.77	32.52		3.5	6.19	100	2.64	1.380	46.23	160
(c) Variation of degree of neutralization											
5 000	2 000	63.74	26.60		3.5	3.44	50	1.32	1.404	36.26	160
		63.74	26.41		3.5	3.37	60	1.58	1.400	36.26	160
		63.74	26.03		3.5	3.23	80	2.11	1.393	36.26	160
		63.74	25.26		3.5	2.96	120	3.17	1.378	36.26	160
(d) Variation of IPDI/HDI content											
5 000	2 000	63.74		90/10	3.5	3.25	100	2.64	1.385	36.26	160
		63.74		80/20	3.5	3.41	100	2.64	1.384	36.26	160
		63.74		70/30	3.5	3.58	100	2.64	1.383	36.26	160
		63.74		60/40	3.5	3.76	100	2.64	1.382	36.26	160
		63.74		50/50	3.5	3.94	100	2.64	1.381	36.26	160
		63.74		25/75	3.5	4.43	100	2.64	1.380	36.26	160
		63.74		0/100	3.5	4.98	100	2.64	1.378	36.26	160
(e) Variation of DMPA											
5 000	2 000	63.74	26.43		2.5	4.06	100	1.88	1.40	36.26	160
		63.74	26.35		3.0	3.58	100	2.26	1.39	36.26	160
		63.74	25.25		4.0	2.61	100	3.01	1.38	36.26	160
		63.74	24.47		5.0	1.65	100	3.77	1.37	36.26	160

We prepared PU anionomers from polyethylene adipate glycol (PEA), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) and dimethylolpropionic acid (DMPA) using a prepolymer mixing process. The prepolymer molecular weight, polyol molecular weight, hard segment content, degree of neutralization, mixed diisocyanates and ionic content were the design variables controlling the property response. From our earlier experience, we noted that a dynamic mechanical response was most sensitive to phase mor-

phology, and we measured dynamic mechanical properties using a Rheovibron.

EXPERIMENTAL

Materials

Polyethylene adipate glycol (PEA, $\bar{M}_n = 1000$ and 2000 g mol^{-1}) was dried and degassed at 80°C and $1\text{--}2 \text{ mmHg}$ for 3 h before use. Dimethylolpropionic

acid (DMPA) was dried at 100°C for 2 h in an oven. Extra pure grades of isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) and dibutyltin dilaurate (DBT) were used as received. Dimethyl formamide (DMF), triethylene tetramine (TETA) and triethylamine (TEA) were dried over 4 Å molecular sieves before use.

Prepolymer synthesis

Basic formulations are given in Table 1. A 500 ml round-bottomed, four-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube and a pipette outlet was used as reactor. Reaction was carried out in a constant-temperature oil bath. PEA, DBT (0.03 wt% based on the total solid) and DMPA dissolved in DMF (5 wt% based on the total charge) were charged into the dried flask. While stirring, the mixture was heated to 80°C for about 30 min, followed by addition of IPDI to the homogenized mixture. The mixture was heated to 80°C for about 3 h to obtain NCO-terminated prepolymers. When mixed diisocyanates were used, HDI was first added to the mixture at 60°C, and after 1 h IPDI was added. The change of NCO value during the reaction was determined using a standard dibutylamine back-titration method.²⁴ Upon obtaining the theoretical NCO value, the prepolymers were cooled to 55°C, and a neutralizing solution, i.e. TEA dissolved in DMF (5 wt% based on the total weight), was added and stirred for 1 h, while maintaining the temperature at 55°C. The 1:1 stoichiometry was obtained by adding TETA at the chain extension step.

Emulsification and chain extension

An aqueous dispersion of PU was obtained by adding water (30°C) to the mixture (55°C). Since the water addition rate is a critical parameter in obtaining a stable dispersion, a pump was used, and water was added for 10 min at a constant flow rate. The phenomena of phase inversion, viscosity, conductivity and isocyanate value change during the emulsification process have been well documented by Dieterich¹ and in our earlier papers.^{25,26} TETA dissolved in water was then fed to the emulsion for a period of 20 min and chain extension was carried out for the next 2 h. The resulting product was a urea-urethane dispersion with a solid content of about 30%, which was stable over six months at room temperature. The procedure for synthesis and dispersion of PU is illustrated in Fig. 1.

Tests

Particle size of dispersions was measured with an Autosizer (Malvern II C). Approximately 0.15 ml of emulsion was diluted with deionized water to an appropriate concentration in the cell, followed by setting the pin hole at

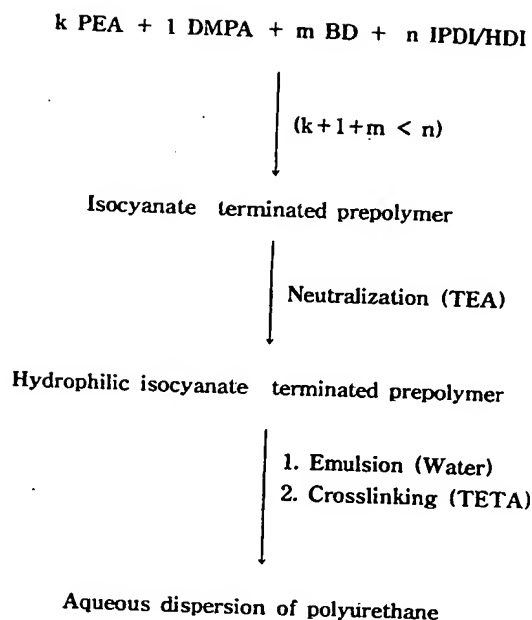


Fig. 1. Procedure for synthesis and dispersion of PU.

200 µm. The z-average diameters were measured at 25°C. The viscosity of the emulsion was measured with a Brookfield viscometer at 25°C.

Tensile properties of the emulsion-cast films were measured using a Tinius Olsen Tensile Tester at a crosshead speed of 500 mm min⁻¹ and an average of at least four measurements was taken. Films were prepared by casting the emulsion on a Teflon plate, followed by drying at 80°C for 5 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mmHg pressure. Microtensile test specimens were prepared according to ASTM D-1822.

Dynamic mechanical tests were performed with a Rheovibron (Orientec, DDV-01FP) from -100°C to 200°C at a frequency of 11 Hz, with a sample size of 0.03 × 0.2 × 3 cm.

RESULTS AND DISCUSSION

Effects of prepolymer molecular weight

This series of experiments was made with a fixed DMPA content (3.5 wt%). The prepolymer molecular weights (M_p) of 3000, 5000 and 7000 were obtained by controlling the [NCO]/[OH] ratio. PEAs of average molecular weight 1250, 1500 and 1750 were prepared by mixing appropriate amounts of PEA1000 (number designates molecular weight) and PEA2000.

Figure 2 shows the particle size and emulsion viscosity of PU ionomer dispersions as a function of M_p . It is seen that particle size decreases and emulsion viscosity increases with increasing M_p . The decreased particle size is due to the easier break-up of the prepolymer solution during emulsification. At constant solid

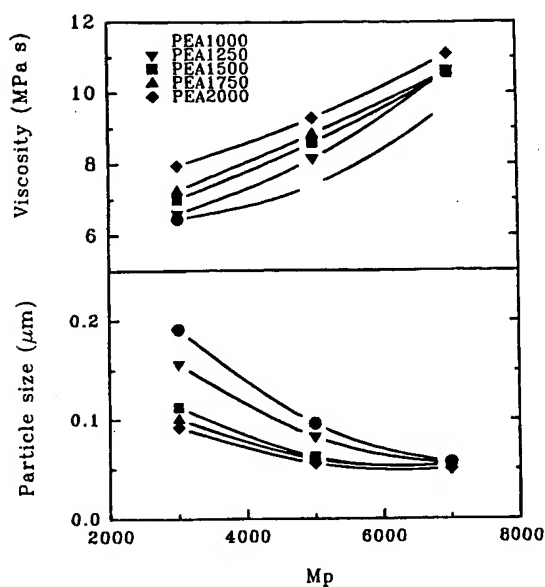


Fig. 2. Emulsion particle size and viscosity as a function of prepolymer molecular weight.

content, the smaller the particle size, the higher the viscosity owing to the increased hydrodynamic volume of the smaller particles. At the same M_p , PU prepared with lower molecular weight PEA gives a larger particle size and smaller emulsion viscosity. This is probably due to intimate phase mixing with low molecular weight PEA, which makes it difficult for anionic centres to leave the surface during emulsification.

Figure 3 shows the dynamic mechanical properties of PUs based on PEA1000 having $M_p = 3000, 5000$ and 7000 (hereafter called 3000 M_p , etc.). With the decrease of M_p , the rubbery plateau becomes well defined and its value generally increases. Since the NCO-terminated PU prepolymers were chain extended with tetrafunctional amine (TETA) in stoichiometric quantity, M_p actually corresponds to the molecular weight between crosslinks. Therefore, with a decrease in M_p , crosslink density increases, i.e. the molecular weight between crosslinks (\bar{M}_c) decreases, leading to the increase in plateau modulus according to:

$$G_N^\circ = \rho RT / \bar{M}_c$$

where ρ , R and T denote density, ideal gas constant and absolute temperature, respectively. With $M_p = 3000$ and 5000, a single broad peak, presumably corresponding to the T_g of the phase-mixed PU, appears at about 45°C. This peak is resolved into a sharp peak at about 25°C and a shoulder around 100°C corresponding to the soft segment rich and hard segment rich phase T_g , for $M_p = 7000$. The prepolymer molecular weight seems to be a useful means to control the microphase separation.

Figure 4 shows the tensile strength and elongation at break of the PU ionomer-cast films as a function of M_p . Tensile strength decreases and elongation at break

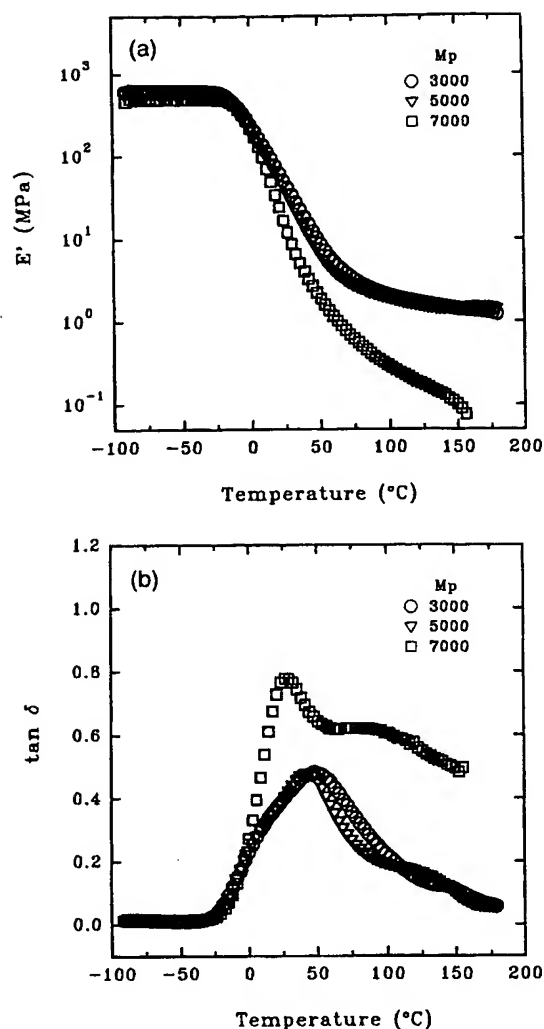


Fig. 3. Dynamic mechanical behaviour of cast films based on PEA1000 as a function of prepolymer molecular weight: (a) storage modulus (E'); (b) $\tan \delta$.

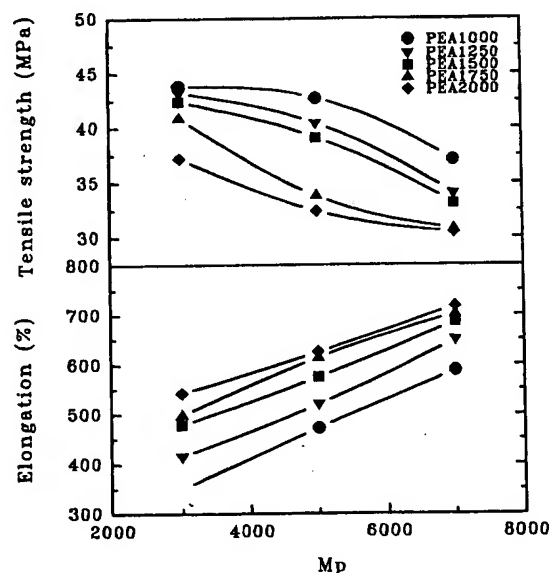


Fig. 4. Tensile strength and elongation at break of cast films as a function of prepolymer molecular weight.

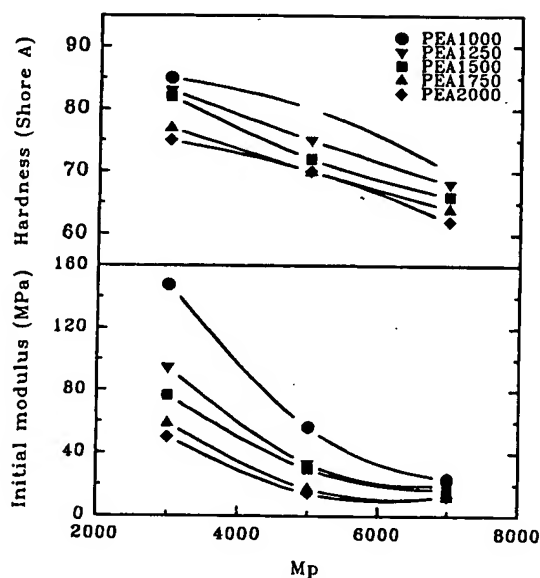


Fig. 5. Hardness and initial modulus of cast films as a function of prepolymer molecular weight.

increases with increase in M_p , and with increase in PEA molecular weight at constant M_p . The decrease in tensile strength and increase in elongation at break with increasing M_p are mainly due to decreased crosslink density. Larger M_p gives a smaller crosslink density giving rise to increased modulus and strength and greater phase separation, which generally gives greater elongation. The effect of PEA molecular weight is similar to the effect of M_p , i.e. increase in PEA molecular weight gives increased extent of phase separation, which gives lower strength and greater elongation.

The effects of M_p on hardness and initial modulus are basically the same as on tensile strength (Fig. 5):

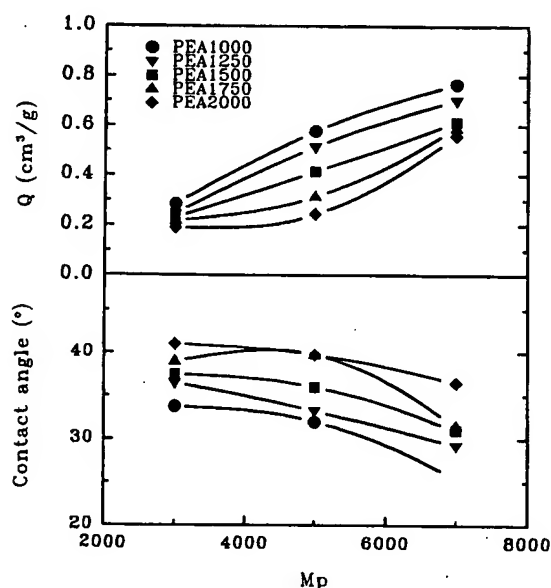


Fig. 6. Swelling coefficient, Q and contact angle of cast films as a function of prepolymer molecular weight.

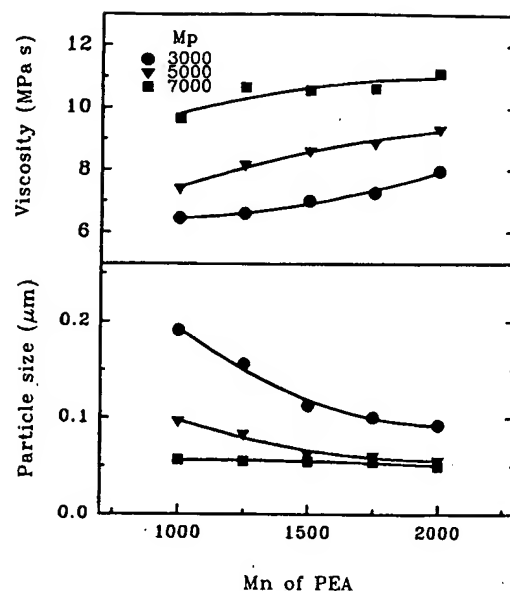


Fig. 7. Emulsion particle size and viscosity as a function of PEA molecular weight.

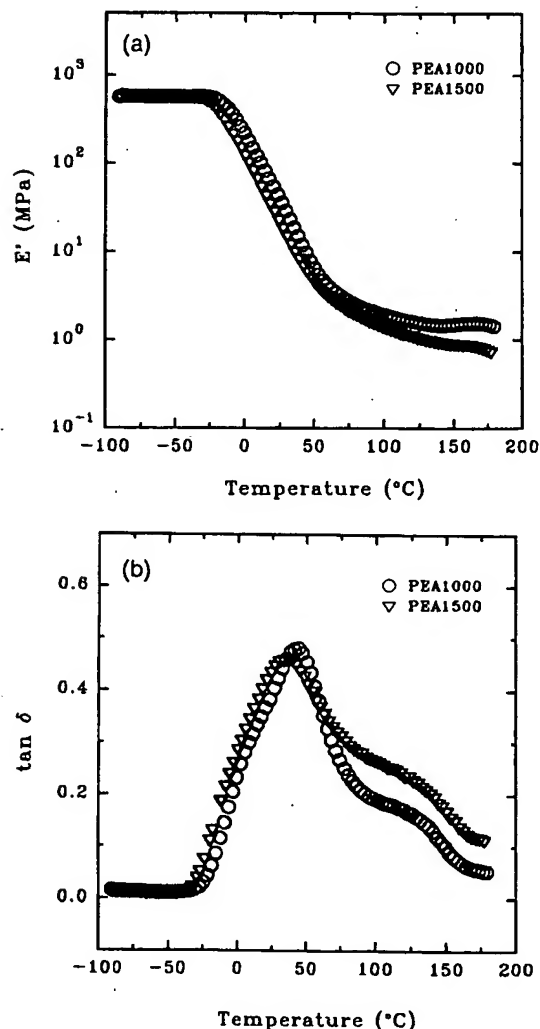


Fig. 8. Dynamic mechanical behaviour of cast films based on 5000 M_p as a function of PEA molecular weight: (a) storage modulus (E'); (b) tan δ .

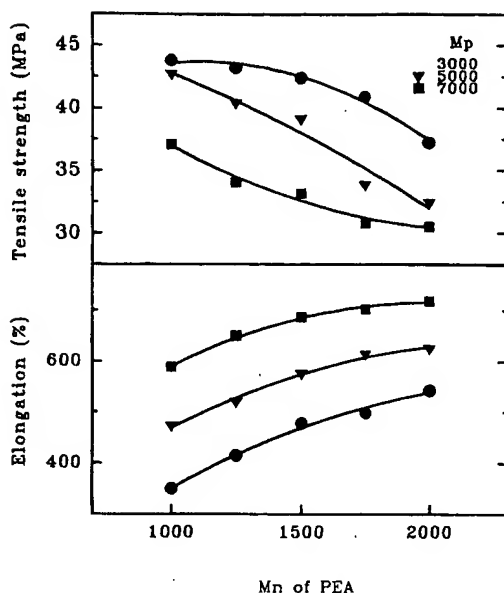


Fig. 9. Tensile strength and elongation at break of cast films as a function of PEA molecular weight.

namely, increase in M_p and PEA molecular weight gives a decrease in hardness and modulus.

Figure 6 shows the swelling coefficients and contact angles of the PU ionomer films as a function of M_p and PEA molecular weight. Swelling coefficient (Q) was determined from:

$$Q = (m - m_0)/m_0 \times 1/\rho_s$$

where m and m_0 are the weight of dry and swollen film, and ρ_s is the density of water. With increasing M_p the contact angle decreases and water swell increases. This is related to the flexibility of the PU chains, which

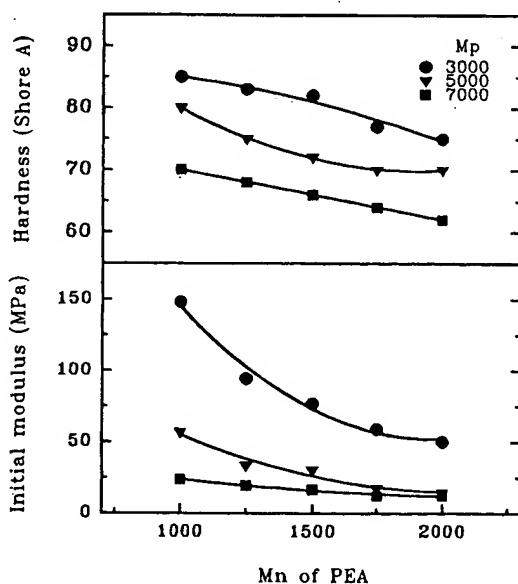


Fig. 10. Hardness and initial modulus of cast films as a function of PEA molecular weight.

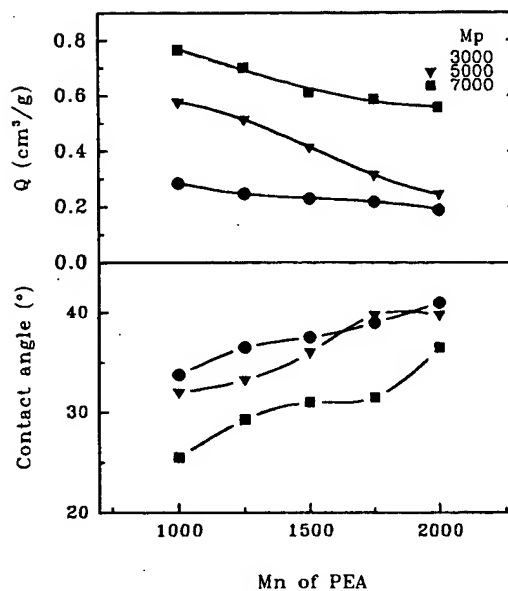


Fig. 11. Swelling coefficient, Q and contact angle of cast films as a function of PEA molecular weight.

allows more of the hydrophilic ionic groups to come to the particle surfaces, which upon coalescence form the surface of the film, resulting in increased affinity with water. On the other hand, increase in PEA molecular weight provides PU with more hydrophobicity leading to an increase in contact angle and decrease in water swell.

Effect of PEA molecular weight

Figure 7 shows the particle size and emulsion viscosity as a function of PEA molecular weight and M_p . Particle size decreases and emulsion viscosity increases due to increased chain flexibility and larger soft segment-hard segment phase separation.

Figure 8 shows the effect of PEA molecular weight on the storage modulus (E') and $\tan \delta$ of 5000 M_p based PU ionomer films. It is seen that lower PEA molecular weight gives a higher storage modulus and a $\tan \delta$ peak at higher temperature. This is probably due to the higher rigidity of PEA1000 based PU as compared with PEA2000 based PU.

Tensile strength decreases and elongation at break increases with increasing PEA molecular weight and increasing M_p due to increased chain flexibility and phase separation (Fig. 9). Hardness and initial modulus decrease with the increase of PEA molecular weight and M_p for the same reason (Fig. 10). Contact angle increases with PEA molecular weight owing to the increased hydrophobicity of PU, and decreases with increase in M_p owing to increased chain flexibility (Fig. 11). Exactly the opposite tendency is observed with water swell, as expected.

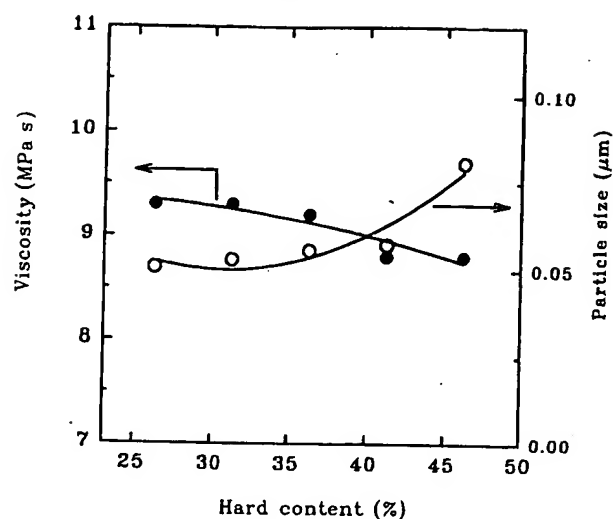


Fig. 12. Emulsion particle size and viscosity as a function of hard segment content.

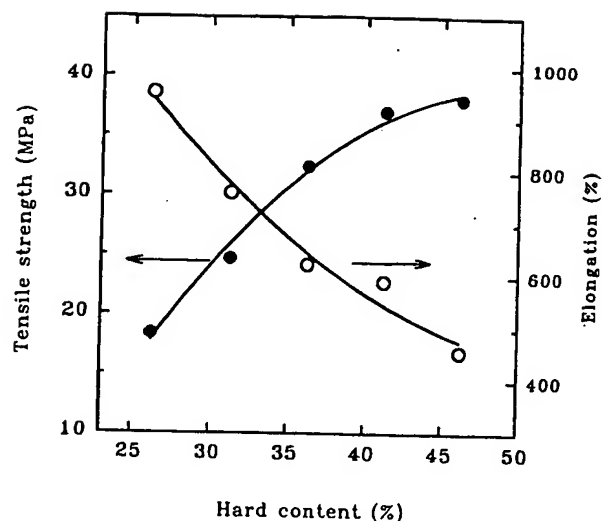


Fig. 14. Tensile strength and elongation at break of cast films based on 5000M_p and PEA2000 as a function of hard segment content.

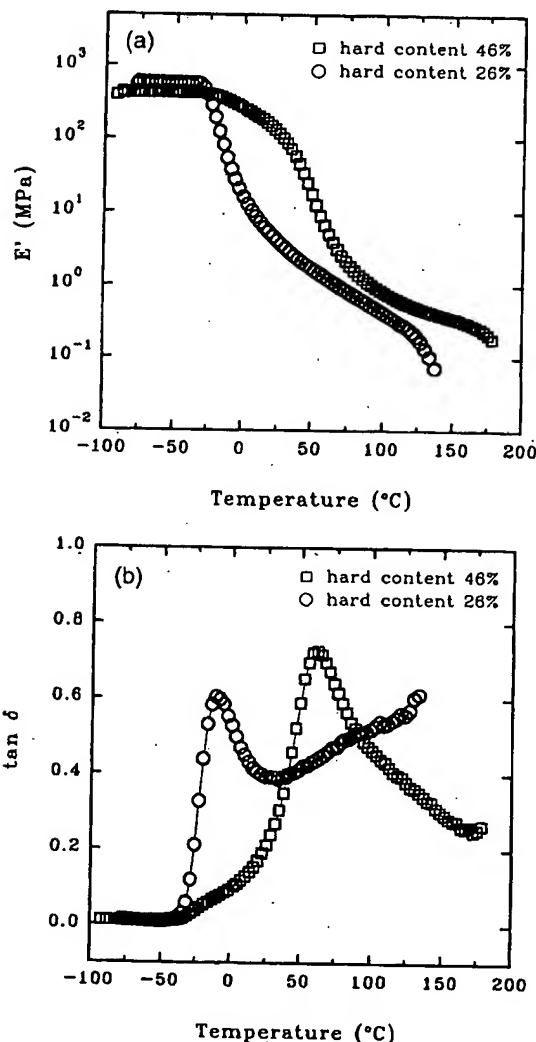


Fig. 13. Dynamic mechanical behaviour of cast films based on 5000M_p and PEA2000 versus hard segment content: (a) storage modulus (E'); (b) $\tan \delta$.

Effects of hard segment content (HSC)

This series of experiments was done at a constant DMPA concentration (3.5 wt%) with PEA2000 and 5000M_p. With increase in HSC, particle size increases and viscosity decreases owing to increased chain rigidity (Fig. 12). However, the change is small since the ionic content is the major parameter controlling the particle size, and it was kept constant. As the HSC increases from 26 to 46%, storage modulus increases and the rubbery plateau becomes well defined and extends to higher temperature (Fig. 13). This implies that hard segments are wholly responsible for load-carrying at elevated temperatures. The $\tan \delta$ peak located at about -20°C is shifted to about 80°C as the HSC increases from 26 to 46%. This implies that soft segment T_g is the

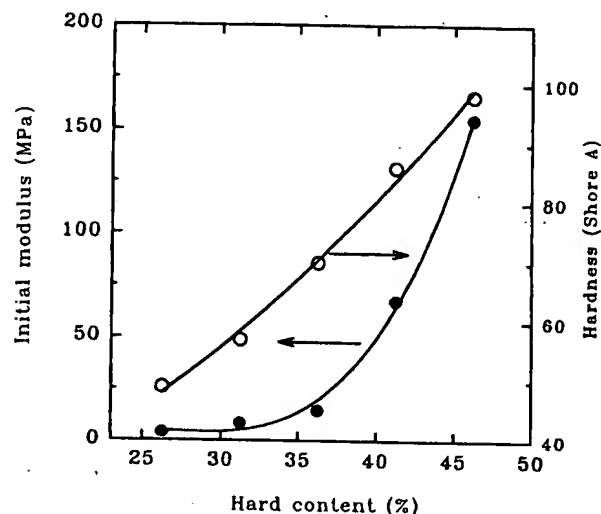


Fig. 15. Hardness and initial modulus of cast films based on 5000M_p and PEA2000 as a function of hard segment content.

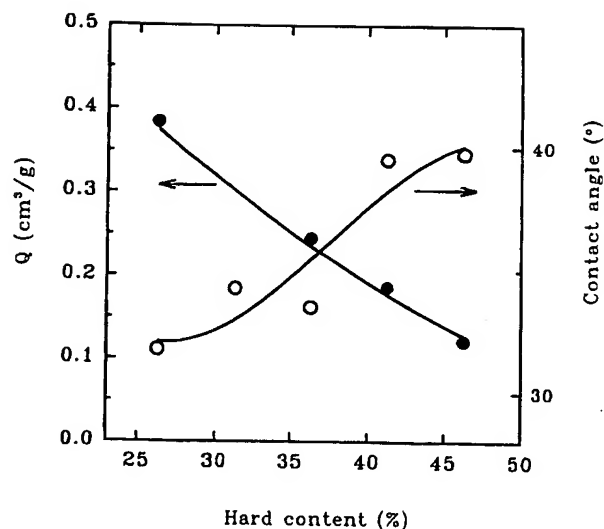


Fig. 16. Swelling coefficient, Q and contact angle of cast films based on 5000 M_p and PEA2000 as a function of hard segment content.

major relaxation at low HSC and hard segment T_g the major relaxation at high HSC.

Hardness, tensile modulus and strength, and contact angle increase and ductility and water swell decrease with increase in hard segment content (Figs 14–16). These changes are mainly due to increased chain rigidity. Contact angle with water is expected to decrease with increasing HSC owing to the increased overall hydrophilicity of the PU. However, the results confirm that chain flexibility is a more significant factor in controlling the contact angle, because chain rigidity does not allow the ionic groups to come to the particle surface.

Effects of ionic content

With increase of ionic content, particle size decreases asymptotically due to increased hydrophilicity, and this leads to a decrease in emulsion viscosity (Fig. 17).

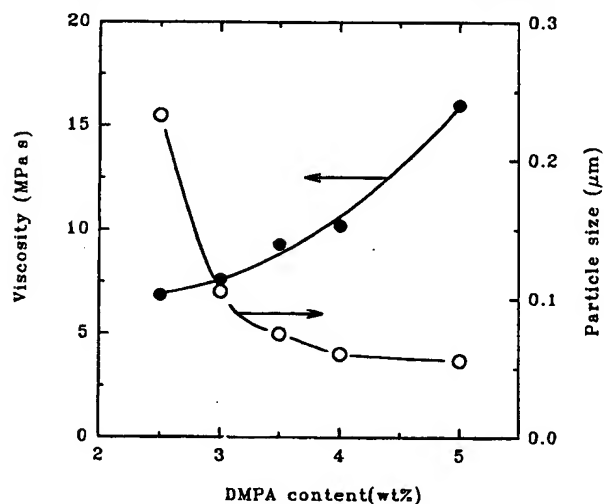


Fig. 17. Emulsion particle size and viscosity as a function of DMPA content.

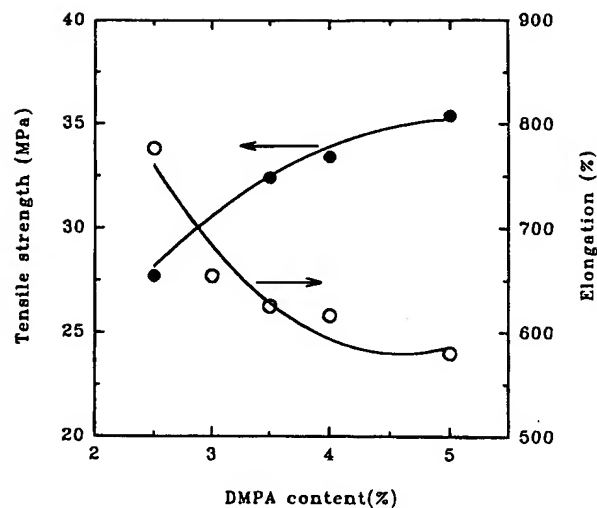


Fig. 18. Tensile strength and elongation at break of cast films based on 5000 M_p and PEA2000 as a function of DMPA content.

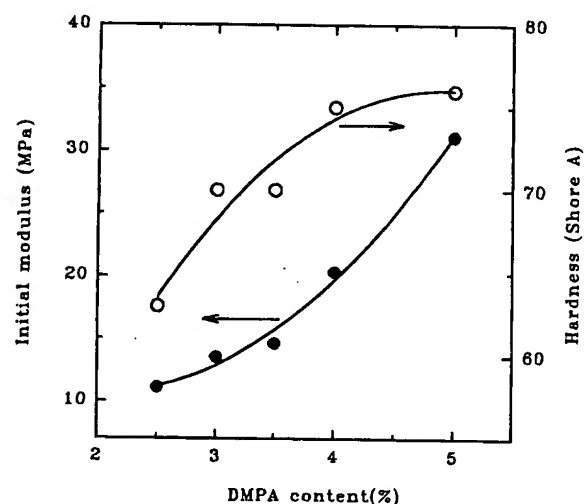


Fig. 19. Hardness and initial modulus of cast films based on 5000 M_p and PEA2000 as a function of DMPA content.

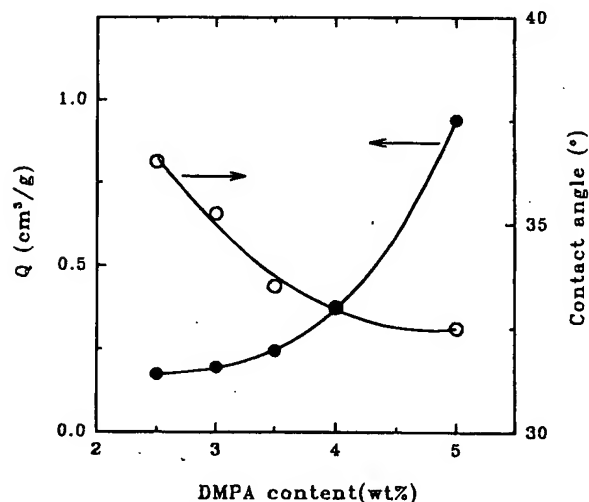


Fig. 20. Swelling coefficient, Q and contact angle of cast films based on 5000 M_p and PEA2000 as a function of DMPA content.

Tensile strength, modulus, hardness and water swell increase, and elongation at break and contact angle decrease with increase of ionic content (Figs 18–20). The increase in tensile properties is ascribed to the increased Coulombic forces between hard segments, and the decreased contact angle to the increased hydrophilicity of the PU.

Effects of the degree of neutralization (DN)

With increase in DN, particle size decreases owing to the increased hydrophilicity of PU because the ionic groups are hydrophilic in nature (Fig. 21). With the increased hydrophilicity, particle size is decreased.

Tensile strength, modulus and hardness increase, and elongation at break decreases with increase in DN (Figs 22 and 23). This is mainly due to the increased Coulombic forces between ionic centres and counterions.

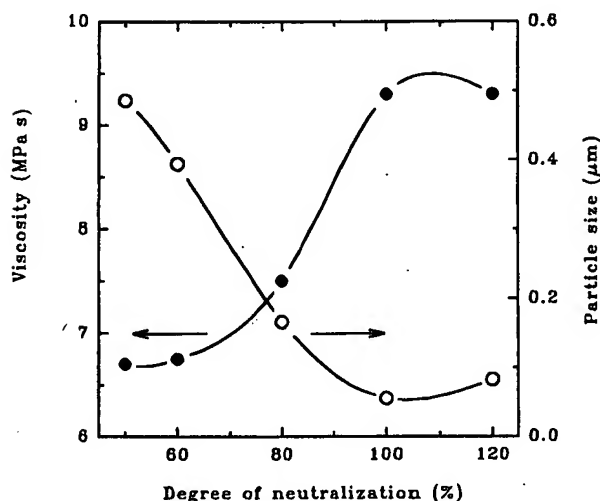


Fig. 21. Emulsion particle size and viscosity as a function of degree of neutralization.

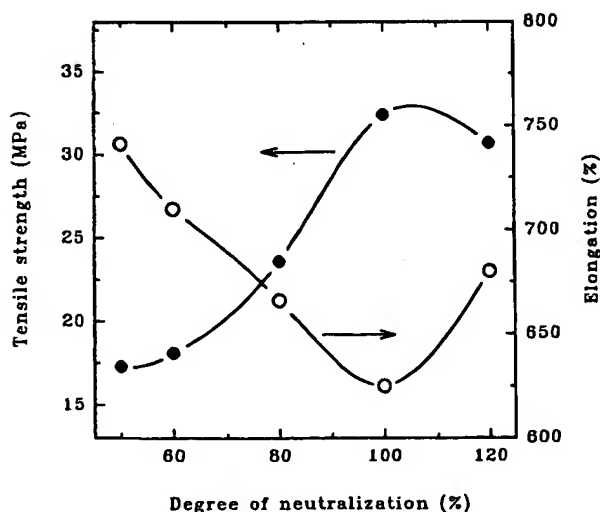


Fig. 22. Tensile strength and elongation at break of cast films based on 5000M_p and PEA2000 as a function of degree of neutralization.

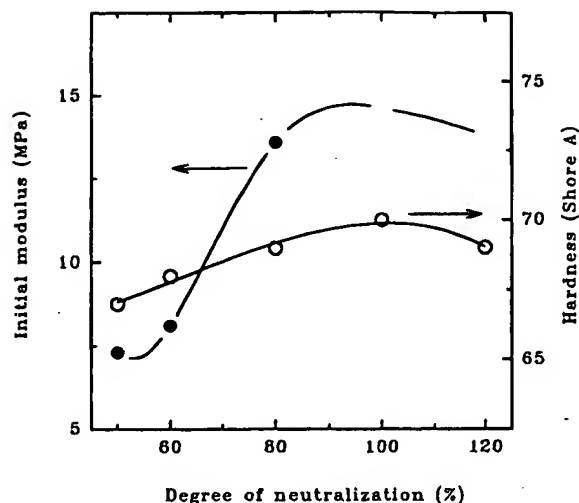


Fig. 23. Hardness and initial modulus of cast films based on 5000M_p and PEA2000 as a function of degree of neutralization.

Effects of mixed diisocyanates

Figure 24 shows particle size and emulsion viscosity as a function of HDI content in the HDI + IPDI system. IPDI gives a much smaller particle size compared with HDI. Particle size increases slowly with addition and increasing HDI content up to 50% of the mixed diisocyanates, beyond which a rapid increase is seen. When the HDI content is relatively small compared with IPDI, the prepolymer termini are mostly capped with IPDI, which is stable in water and allows almost quantitative crosslinking with TETA in the process of dispersion. However, when the amount of HDI is relatively large compared with IPDI, the prepolymer termini are likely to be capped with HDI, which allows reactions with water, and hence chain extension by TETA is not

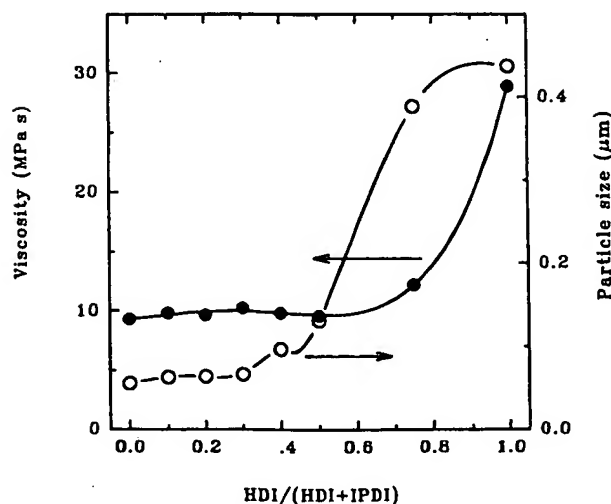


Fig. 24. Emulsion particle size and viscosity in mixed diisocyanate system.

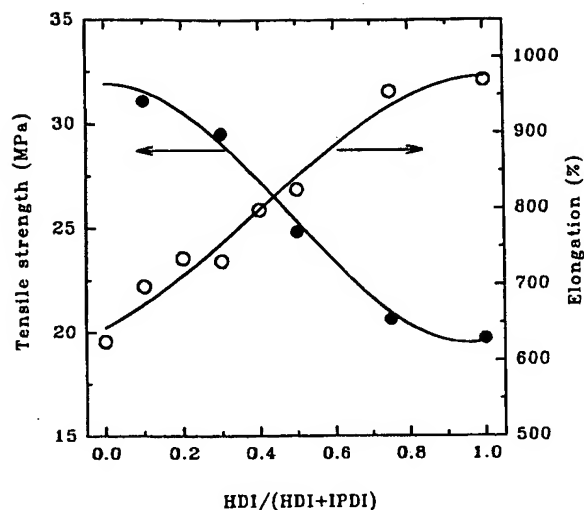


Fig. 25. Tensile strength and elongation at break of cast films based on 5000M_p and PEA2000 in mixed diisocyanate system.

qualitative. This leads to swelling by water and increased particle size. Surprisingly, the emulsion viscosity remains at the level of IPDI in the mixed diisocyanate system.

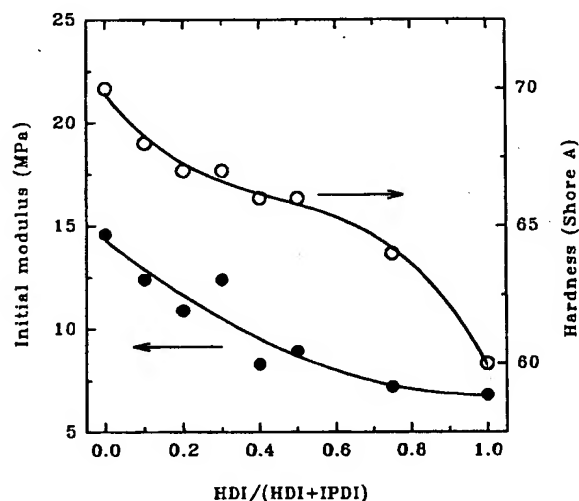


Fig. 26. Hardness and initial modulus of cast films based on 5000M_p and PEA2000 in mixed diisocyanate system.

Tensile strength, modulus and hardness decrease with the increase in HDI owing mainly to the flexible nature of HDI as compared with IPDI (Figs 25 and 26).

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